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(54) **Hydrophillic polyurethane composition**

(57) Water absorptive polyurethane composition, having high mechanical strength, is formed of A. about 25% to about 75% of a hydrophilic polyether polyurethane which is the reaction product of diethylene glycol and a polyoxyethylene glycol having a molecular weight of about 1000 to about 8000 with a polyisocyanate and B. about 75% to about 25% of a hydrophobic polyester polyurethane which is the reaction product of a polyfunctional polyester derived from the condensation of a polyol with a polybasic acid with a polyisocyanate.

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HYDROPHILIC POLYURETHANE COMPOSITION

This invention relates to polyurethanes and in particular to hydrophilic polyether polyurethanes having improved mechanical properties.

5 Hydrophilic polyurethane polymers having high water absorptivity can be produced by reacting a polyethylene ether glycol with a polyisocyanate. However, the mechanical properties of such polyurethanes in the wet state could be further improved.

10 It has now been discovered that hydrophilic polyether polyurethanes having excellent mechanical properties in the wet state can be realized by blending such polymers with prescribed amounts of a hydrophobic polyester polyurethane and the provision of these hydrophilic polyurethane polymer blends together with
15 their preparation and uses constitutes the principal object and purpose of the invention.

 The hydrophilic polyurethane composition of the invention comprises by weight and on a 100% basis a
20 blend of A. about 25% to about 75% of a hydrophilic polyether polyurethane which is the reaction product of diethylene glycol and a polyethylene ether glycol having a molecular weight of from about 1000 to about 8000 with a polyisocyanate and B. about 75% to about 25% of
25 a hydrophobic polyester derived from the condensation of a polyol with a polybasic acid with a polyisocyanate.

 Surprisingly, the polymer blend retains desirable hydrophilic surface property being essentially comparable in this respect to the hydrophilic polyether polyurethane component. Yet, at the same time, the presence of the hydrophobic polyester polyurethane results in a marked increase in the tensile strength of the polymer blend in the wet state. Typically, the increase in tensile strength becomes significant when the
35 composition of the blend approaches 25% polyether and 75% polyester, rising to a maximum between these values

and then falling back to the beginning concentration, giving rise to a bell curve. Such behavior is unexpected and as yet has not been explained. Additionally, the polymer blends exhibit good hardness, both in
5 the dry and wet stage as measured by the Durometer A Hardness Test. A further desirable property is the reduced swelling of the blends as compared to the hydrophilic polyether polyurethane per se.

The hydrophilic polyurethane blends herein are
10 prepared by forming a mixture of the hydrophilic polyether polyurethane and hydrophobic polyester polyurethane employing mixing techniques familiar in the art. In a typical procedure, the requisite amounts of the polyether and polyester polymers are dissolved
15 in a solvent. The resulting solution can then be applied to a suitable substrate and after evaporation of the solvent, a film of the polymer blend is obtained. Exemplary solvents include chloroform, cyclohexanone, diethylformamide, tetrahydrofuran, dimethylsulfoxide, lower aliphatic ketones such as acetone,
20 methylethyl ketone, lower saturated, aliphatic alcohols, for example, 1 to 4 carbon atoms and the like, including mixtures of such solvents. For casting films, the solution may contain by weight from about 5% to about 10% solids while for dipping the solids content is about 3% to about 5%.

The polymer blends may also be formed by mixing finely divided polyether and polyester polyurethanes of the invention in an extruder and extruding into the
30 desired structure or configuration.

The hydrophilic polyether polyurethane component of the herein polyurethane is prepared by reacting a major amount of a polyoxyethylene glycol having a molecular weight of from about 1000 to about 8000 or mix-
35 tures thereof, a minor amount of diethylene glycol and a polyisocyanate. Exemplary polyoxyethylene glycols are the various commercial Carbowaxes available in a

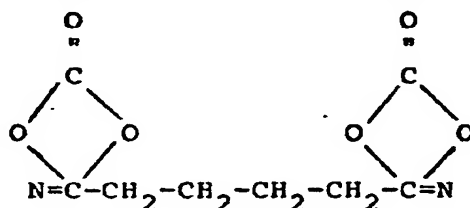
range of molecular weights from the Union Carbide Corporation. Representative Carbowaxes are PEG (CARBOWAX 1450^R) and PEG (CARBOWAX 8000^R) in which the numbers refer to molecular weights. The proportions in which the long-chain polyglycol and the low molecular weight diethylene glycol are present in the polyether polyurethane will determine its degree of hydrophilic character. Increasing the molecular weight of the long-chain polyethylene glycol and/or the amount thereof promotes strong hydrophilic properties to the final product. Lessened hydrophilic character results by increasing the proportion of low molecular weight glycol, that is, diethylene glycol. Generally speaking, the polyether polyurethane is proposed from about 45% to 85% of the polyoxyethylene glycol, about 2.25% to 11.0% diethylene glycol and about 15% to 40% of the polyisocyanates.

The polyisocyanate used in making the hydrophilic polyether polyurethane component of the herein polyurethane blends may be represented by $R(NCO)_n$ wherein n is greater than 1, preferably 2-4, and R is an aliphatic, alicyclic, aliphatic-alicyclic, aromatic, or aliphatic-aromatic hydrocarbon compound of from 4 to 26 carbon atoms, but more conventionally from 6 to 20 and generally from 6 to 13 carbon atoms. Representative examples of the above isocyanates are: tetramethylene diisocyanate; hexamethylene diisocyanate; trimethylhexamethylene diisocyanate; dimer acid diisocyanate; isophorone diisocyanate; diethylbenzene diisocyanate; decamethylene 1,10-diisocyanate; cyclohexylene 1,2-diisocyanate and cyclohexylene 1,4-diisocyanate and the aromatic isocyanates such as 2,4- and 2,6-tolylene diisocyanate; 4,4-diphenylmethane diisocyanate; 1,5-naphthalene diisocyanate; dianisidine diisocyanate; tolidine diisocyanate; a polymeric polyisocyanate such as neopentyl tetra isocyanate; m-xylylene diisocyanate; tetrahydronaphthalene-1,5 diisocyanate; and bis(4-iso-

cyanatophenyl)methane.

The preferred isocyanate is methylene di(cyclohexyl isocyanate). Other but slightly less preferred diisocyanates are trimethyl hexamethylene diisocyanate and isophorone diisocyanate.

Other compounds which are useful are the isocyanate equivalents which produce the urethane linkages such as the nitrile carbonate, that is, the adiponitrile carbonate of the formula:



In preparing the hydrophilic polyether polyurethane component, the glycols and the polyisocyanate are reacted in the presence of known catalysts for such reaction and in this connection mention is made of tin salts and organic tin esters, for example, dibutyltin dilaurate, tertiary amines such as triethyl diamine (DABCD), N,N,N',N'-tetramethyl-1,3-butane diamine and other recognized catalysts for urethane reactions known in the art.

The hydrophobic polyester polyurethane components of the herein polymer blends are generally known polymer entities, the description and preparation of which are set forth in the technical and patent literature. They are obtained by condensing a polyisocyanate with a polyester resin precursor having two or more active hydrogens in the known manner of preparing polyurethane polymer. These polyesters can be regarded as the esterification product of a polybasic carboxylic acid with a polyol having multiple OH groups such as polymeric diols. Examples of these diols aforesaid are polytetramethylene ether glycol, propylene oxide based polyols as well as propylene/ethylene oxide block copolymers. The polybasic acid is commonly a polycar-

boxylic acid of which the more familiar members include adipic acid, melletic acid, pyromellitic acid, trimellitic acid, succinic acid, itaconic acid, maleic acid, fumaric acid, mesaconic acid, azelaic acid, pimelic and the like. A polyester resin will be selected which when reacted with a polyisocyanate will yield a polyester polyurethane which exhibits little or no propensity to absorb water. A hydrophobic polyester polyurethane will normally be produced when the polymeric diol contains oxyalkylene units having 3 or more carbon atoms, for example, oxypropylene.

The hydrophilic polyurethane polyene compositions of the present invention are dimensionally stable upon repeated exposure to boiling water and have unique physical properties that are of advantage when used in the manufacture of soft contact lens.

The above described hydrophilic polyurethane polyene resin compositions are also useful as coatings, molding compounds, absorbents, controlled release agents, ion exchange resins, and in the manufacture of dialysis membranes, dentures, cannulae, contact lenses, packaging components, burn dressings, contraceptive devices, sutures, surgical implants, blood oxygenators, intrauterine devices, vascular prostheses, oral delivery systems, battery separator plates, eye bandages, corneal prostheses, antifog coatings, surgical drapes, oxygen exchange membranes, artificial finger nails, finger cots, adhesives, gas permeable membranes, and in protective and drag resistant coatings.

The invention is further illustrated by the following examples, in which the components are in parts by weight unless stated otherwise.

Preparation of Polyether Polyurethane

Example I

A mixture of 49.0 parts of CARBOWAX 1450^R (a polyethylene glycol having a number average molecular weight of 1450, sold by the Union Carbide Corporation,

New York, New York 10017) and 11.0 parts of diethylene glycol were heated to about 70°C with stirring until a homogeneous melt was obtained. While continuing the stirring, there was added 40.0 parts of methylene bis-cyclohexyl-4,4-isocyanate (a product sold as DESMODUR W^R by the Mobay Chemical Corporation, Penn Lincoln Parkway West, Pittsburgh, Pennsylvania 15205) during which the temperature decreased. When the temperature reached about 50°C, there was added 0.15 ml of stannous octoate, (a product identified as T₉ and manufactured by Metal and Thermite Company of Rahway, New Jersey) and the mass allowed to exotherm to about 70°C. The mass was then poured into a polypropylene pan. During pouring, the temperature continued to rise to about 80°C and the mass foamed. Upon finishing of the pouring operation, the pan was placed in an oven and held at 100°C for about one hour to complete formation of the polymer.

Preparation of Polyether/Polyester Urethane Blends
and Products Containing Them

The polyether polyurethane and a polyester polyurethane were dissolved in chloroform and the resulting solution used to prepare films of the polymer blend. The polyester polyurethane is obtained by the condensation of toluene diisocyanate with a polyester polyol derived from a dicarboxylic acid having 6 to 10 carbon atoms and an alkylene diol of 3 to 4 carbon atoms. Essentially equal amounts of the diisocyanate and polyester polyol are present. Films of the polymer blend were cast by applying the solvent solution aforesaid to a suitable substrate and the solvent allowed to evaporate. Films were also formed by immersing a mandrel of the requisite shape into the solvent solution, the mandrel withdrawn and the solvent allowed to evaporate. Mandrels were used to form gloves, finger cots and condoms. For casting films, the solution may contain from about 5% to 10% solids while for dipping the solution

may contain 3% to 5% solids.

Blends can also be prepared from the solid polymers by mixing finely divided particles thereof in an extruder from which the polymer blend is extruded in the desired shape such as a nasal gastric tube, cannula or a film.

The polyether/polyester polyurethane blend aforesaid may be mixed with or used to encapsulate drugs or other medicament to provide controlled release thereof when placed in an aqueous or saline solution or in body fluids. The drug delivery can be of any convenient shape, for example, tablets for oral ingestion implants, suppositories, etc.

In preparing the above described polymer blends, the polyether polyurethane will be from about 25% to about 75% and the polyester polyurethane about 75% to about 25%.

Example II

The procedure of Example I was repeated except the polyether polyurethane was made from the following components:

PEG (CARBOWAX 8000 ^R)*	41.0 parts
Diethylene Glycol	9.0 parts
DESMODUR W ^R	33.0 parts
Stannous Octoate (T ₉)	0.15 ml

Example III

The procedure of Example I was repeated except the polyether polyurethane was made from the following components:

PEG (CARBOWAX 8000 ^R)*	82.0 parts
Diethylene Glycol	3.0 parts
DESMODUR W ^R	15.0 parts
Dibutyl Tin Dilaurate (T ₁₂)	0.20 ml

*a polyethylene glycol having a number average molecular weight of 7500-8000 and sold by the Union Carbide Corporation.

The polyether/polyester blends were immersed in

water at room temperature for 24 hours, then removed and wiped with paper toweling to remove surface water. The percent water content was determined from the gain in weight of the sample. The Durometer A Hardness was measured on dry and wet samples. Tensile strength was measured on both dry and wet samples.

The polyether/polyester polyurethane of the Examples were further tested for water uptake by means of the following procedure. A sample was heat extruded at about 300°C to form tubing, 0.25 cm in diameter and 0.058 cm wall thickness. Short lengths of the tubing samples (4 cm long) were weighed, the diameter and wall thickness were measured in the dry states. Samples were placed in water at room temperature for 24 hours, external water removed, the weight, diameter and wall thickness determined and the change in volume calculated. The percent water uptake, diameter, wall thickness and volume changes are calculated by the formula

$$\frac{x_w - x_d}{x_d} \times 100$$

The water uptake of the polymer blends was essentially the same as the hydrophilic polyether polyurethane per se but with much improved mechanical strength in the state.

CLAIMS

1. A water absorptive polyurethane composition comprising a blend of two polyurethane polymers in which the first polymer, A, is a hydrophilic polyether polyurethane formed by the reaction of diethylene glycol and a polyoxyethylene glycol having a molecular weight of 1000 to 8000 with a polyisocyanate, the second polymer, B, is a hydrophobic polyester polyurethane formed by the reaction of a polyfunctional polyester, derived from the condensation of a polyol and a polybasic acid, with a polyisocyanate and in which the blend contains from 25% to 75% by weight of the first polymer A and the remainder of the second polymer, B.

2. A water absorptive polyurethane composition as claimed in Claim 1 in which the first polymer is formed by the reaction of from 2.25% to 11% by weight of diethylene glycol and 45% to 85% by weight of the polyoxyethylene glycol with from 15% to 40% by weight of a polyisocyanate.

3. A water absorptive polyurethane composition as claimed in either Claim 1 or Claim 2 in which the polyoxyethylene glycol has a molecular weight of 1450.

4. A water absorptive polyurethane composition as claimed in either Claim 1 or Claim 2 in which the polyoxyethylene glycol has a molecular weight from 7500 to 8000.

5. A water absorptive polyurethane composition as claimed in any of the preceding Claims in which the polyisocyanate is methylene di(cyclohexyl isocyanate).

6. A water absorptive polyurethane composition as claimed in any of the preceding Claims in which the blend contains 40% by weight of the first polymer, A, and 60% by weight of the second polymer, B.

7. A water absorptive polyurethane composition as claimed in any of the Claims 1 to 4 in which the blend contains 60% by weight of the first polymer, A, and 40% by weight of the second polymer, B.

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8. A water absorptive polyurethane composition as claimed in any of the preceding Claims in which the second polymer is formed by the reaction of a polyfunctional polyester, derived from the condensation of an aliphatic diol and a dicarboxylic acid, with a polyisocyanate.

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9. A water absorptive polyurethane composition as claimed in Claim 8 in which the aliphatic diol is an alkylene diol having 3 or 4 carbon atoms, the dicarboxylic acid has from 6 to 10 carbon atoms and the polyisocyanate is toluene diisocyanate.

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10. The method of making a water absorptive polyurethane composition as claimed in Claim 1 wherein the first polymer, A, and the second polymer, B, are blended by forming a solution of the polymers in a solvent or solvent mixture.

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11. The method as claimed in Claim 10 wherein the composition is prepared as a film by casting the solution on a substrate or dipping a mandrel in the solution and thereafter evaporating the solvent.

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12. An article comprising a film of a composition as claimed in any of the Claims 1 to 9.

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13. An article as claimed in Claim 12 in which the film contains a medicament.

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14. An article as claimed in Claim 13 in which the medicament is a hormone.

15. An article as claimed in Claim 13 in which the medicament is a steroid.

16. A burn dressing comprising a film as claimed in any of the Claims 12 to 15.

17. A moisture-vapor permeable membrane comprising a film as claimed in claim 12.

18. A dialysis membrane comprising a film as claimed in claim 12.

19. A surgical drape comprising a film as claimed in claim 12.

20. A molded or extruded article formed from a water absorptive polyurethane composition as claimed in any of the claims 1 to 9.

21. A cannula comprising an extruded composition as claimed in Claim 20.

22. A cannula as claimed in Claim 21 in which the the composition contains a medicament.

23. An interuterine device comprising a molded composition as claimed in any of the Claims 1 to 9.

24. An interuterine device as claimed in Claim 23 in which the composition contains a contraceptive composition.

25. An ophthalmic contact lens comprising a molded composition as claimed in any of the Claims 1 to 9.

26. A corneal prosthesis comprising a molded composition as claimed in any of the Claims 1 to 9.

27. An oral delivery system comprising a composition as claimed in any of the claims 1 to 9 enclosing a pharmacologically active agent.

5 28. Water absorptive polyurethane compositions as claimed in Claim 1 and articles fabricated therefrom as herein described.

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